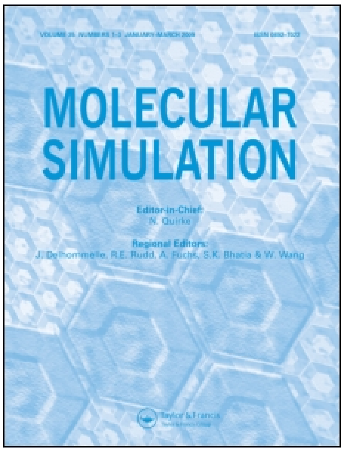

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Towards the engineering of enantioselective properties of supported platinum catalysts

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Towards the engineering of enantioselective properties of supported platinum catalysts

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Understanding the sub-molecular structure of conformationally complex adsorbed molecules is still a difficult task for experimentalists interested in the structure of modified surfaces, therefore first principles calculations can be a fundamental tool for the investigation of structural details otherwise impossible to identify. Density functional theory (DFT) calculations of the adsorption of cinchonidine (CD) and *O*-phenyl-cinchonidine (OPhCD) have been performed, using large metal clusters to simulate the metal surface and a zero order regular approximation (ZORA) Hamiltonian to account for relativistic effects due to the heavy nuclei involved. The local geometry of chiral surface sites formed by CD was investigated in detail and discussed in relation to the reaction of enantioselective hydrogenation of activated ketones on cinchona modified platinum. Also, the relevant conformations of OPhCD were investigated and the resulting structure of the chiral sites is discussed and compared to those obtained for the parent alkaloid CD. The adsorption behavior on platinum of a series of substituted anisoles was also investigated, in order to evince the effect that phenyl substitution might have on the relative proportion of surface conformers in substituted OPhCD ethers, that have been shown to possess interesting enantioswitching properties when used as surface modifiers in the enantioselective hydrogenation of activated ketones on cinchona alkaloid modified platinum. A correlation between conformational distribution of the modifiers and the selectivity of the catalyst is proposed.

Keywords: Enantioselective heterogeneous catalysis; Density functional theory; Cinchona alkaloids; Enantioselective hydrogenations; Chiral surfaces; Chiral switches

1. Introduction

Catalysis is typically divided in two broad fields: homogeneous, where both catalyst and reactant are in the same phase and heterogeneous, where the reaction occurs at the interface between two separate phases. Heterogeneous catalysis has the remarkable advantage that separation and reuse of the catalyst is technically less demanding, often implying a simple filtration when the substrate is in the liquid phase. For the same reason, a more efficient recovery of the final product is also achievable. This is of course a basic issue for large-scale chemical processes, but is also of great interest in the production of fine chemicals, when a catalytic step is involved. In this case, if the desired molecule is chiral, it is highly desirable to possess catalysts able to deliver the final product with the correct handedness. Unfortunately only few such catalytic systems are known, of which by far the better studied are the nickel–tartrate catalyst for the enantioselective hydrogenation of β-ketoesters and the cinchona alkaloid modified platinum for the enantioselective hydrogenation of α-ketoesters [1]. The latter is the most studied and the scope of its applications has been broadened in the past years to include α-ketoesters and α-hydroxyesters [2], α,α,α-trifluoromethyl ketones [3], α-ketoamides [4,5], α-diketones [6], ketopantolactone [7] and α-ketoacetals [8,9]. Furthermore besides platinum also palladium and rhodium have been modified by cinchona alkaloids, leading to promising results in the enantioselective hydrogenation of C—C and C—O double bonds [13–16]. Several recent reviews report the state of research in this field [10–12]. An interesting feature of the Pt/cinchona catalyst is that modifiers competing for adsorption sites can give rise to rapid changes (switching) of the enantioselective properties of the metal surface [17]. By using *O*-phenyl substituted cinchonidines (OPhCD) (scheme 1), the sense of enantioselectivity imparted by modified platinum can be dynamically switched, although all modifiers involved possess the same absolute configuration. In other words, chemical variations to the

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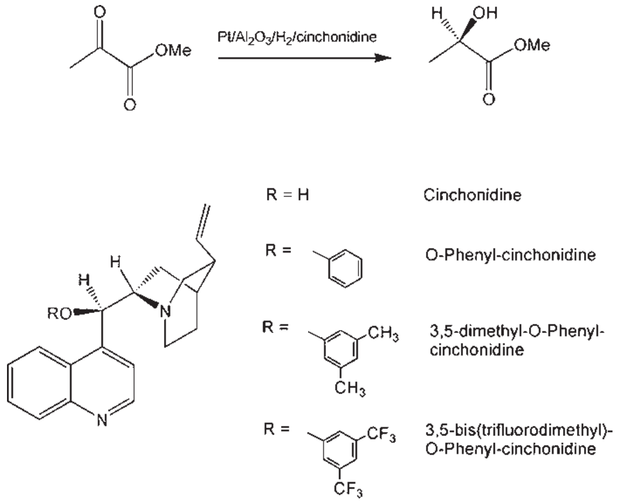


Scheme 1. CD and OPhCD ethers.

structure of the modifier leads to effective tuning of the chiral sites generated on a metal surface. Such features indicate that modification of reactive surfaces can be engineered, to obtain tailored catalytic systems, or more in general tunable properties of solid-liquid interfaces. Evidently, uncovering the mechanism would be of fundamental help to define scopes and limits of this catalyst, but the lack of suitable spectroscopic techniques renders the task very complex and several proposals yet coexist in the competent literature [10,11]. Nonetheless a rather wide agreement is found on a fundamental point, namely that the modifier molecule is adsorbed on the metal surface thus generating surface chiral sites within which enantioselectivity occurs. The structure of such sites has been investigated by using several approaches: isotope exchange [18], structure and reactivity correlations with synthetic modifiers [19], systematic variation of the substrate substituents [20,21], attenuated total reflection (ATR) infrared spectroscopy [22,23], scanning tunneling microscopy (STM) [24] and molecular modelling [25–27]. The following report illustrates the latest results obtained by computational modeling of the interaction between the modifier (cinchonidine (CD) or substituted CD) and a Pt(111) surface, by means of density functional theory (DFT) calculations.

2. Computational methods

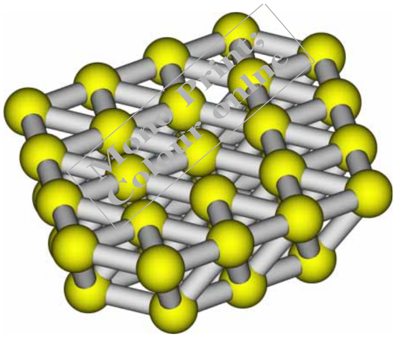


Figure 1. The platinum 38 cluster used for simulation of a platinum surface.

Adsorption studies have been performed using the platinum cluster shown in figure 1 formed by 38 platinum atoms to simulate a Pt(111) surface. All the cluster calculations have been performed using the Amsterdam density functional (ADF) program package [28]. A frozen core approximation was used for the inner core of all the atoms. The orbitals up to 1s were kept frozen for all second row elements, while orbitals up to 4f were kept frozen for platinum. Decreasing the Pt frozen core to 4d, which implies the explicit calculation of 14 additional electrons per platinum atom, has been shown to increase the adsorption energy by only about 5 kJ/mol for the adsorption of benzene [29]. The importance of relativistic effects has been shown for calculations involving platinum [30,31]. It was shown that the scalar relativistic correction could account for up to 70% of the total energy in the adsorption of carbon monoxide on platinum and that also the calculated adsorption site is influenced by the use of a relativistic correction [30]. The core was modeled using a relativistically corrected core potential created with the DIRAC utility in the ADF program. The DIRAC calculations imply the local density functional in its simple X-α approximation without any gradient corrections, but the fully relativistic Hamiltonian is used, including spin–orbit coupling. The relativistic scalar approximation (mass–velocity and Darwin corrections) was used for the Hamiltonian, with the zero order regular approximation (ZORA) method [32], where spin–orbit coupling is included already in zero order. The first order Pauli formalism [33] was shown to have theoretical deficiencies due to the behaviour of the Pauli Hamiltonian at the nucleus, which lead to variational collapse [34] for increasing basis set size. The ZORA formalism requires a special basis set, to include much steeper core like functions that are implemented in the code. Within this basis set the double-ζ (DZ) basis functions were used for platinum, and double-ζ plus polarization (DZP) basis functions for second row elements. The local part of the exchange and correlation functional was modeled using a Vosko *et al.* [35] parametrization of the electron gas. The non local part of the functional was modeled using the Becke correction [36] for the exchange and the Perdew correction [37] for the correlation. All calculations were run unrestricted. The bond distance for the platinum was fixed to the experimental value of 2.775 Å for bulk metal [38]. Quinoline, the anchoring moiety of the alkaloid, was initially placed on a double bridge site, in agreement with the finding that bridge sites are the most stable for benzene on a Pt(111) surface [29,39,40]. Since the hollow sites were found to be second in order of stability, double hollow sites were tested in a recent study as possible adsorption sites for CD. It was shown that they are unstable and lead to double bridge sites [27]. All degrees of freedom of the adsorbed alkaloids were set free to optimize. Several studies dedicated to the adsorption of organic molecules on platinum clusters have pointed out that relaxation of the interacting part of the cluster results in an increase of adsorption energy [29,40,41]. This approximately accounts for the changes induced on a surface by the strong binding of adsorbates. It has also been shown that using a Pt 31 cluster for the calculation of adsorption energies the effect of cluster relaxation is almost exactly compensated by the energy contribution due to the basis set superposition error (BSSE) [41]. This latter correction tends in fact to decrease the adsorption energy. Due to this compensation, in the present study both cluster relaxation and BSSE correction have been neglected in first approximation. The comparison of the energies of the surface conformers was done by setting to zero the energy (total electronic energy) of the reference structure surface closed(1) (SC(1)) and then evaluating the differences between the reference and other calculated structures. Adsorption energies were calculated with respect to the Open (3) conformer of CD and OPhCD, using the following equation:

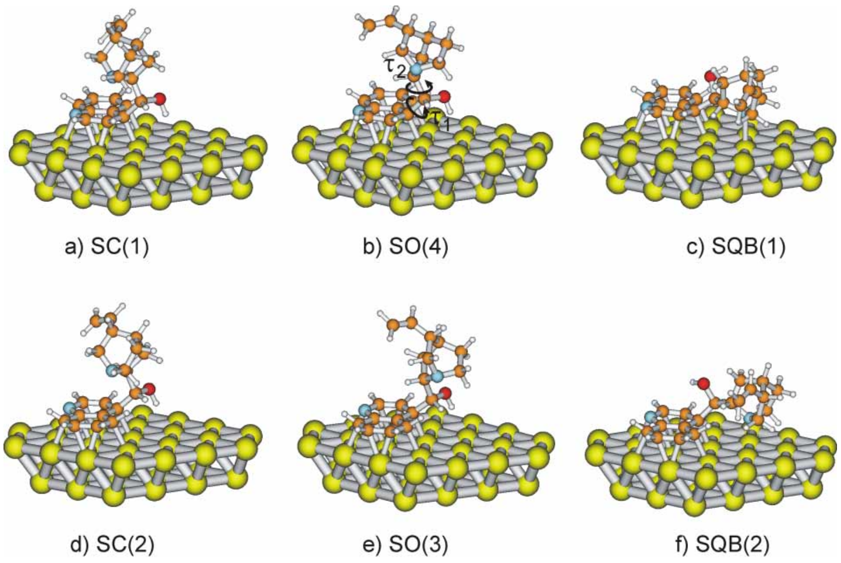
$$\Delta E_{\text{Ads.}} = E_{\text{Cluster+Adsorbate}} - E_{\text{Cluster}} - E_{\text{Free Molecule}}$$

where $E_{\text{Cluster + Adsorbate}}$ is the energy of the cluster with the molecule adsorbed, E_{Cluster} is the energy of the isolated cluster and $E_{\text{Free Molecule}}$ is the energy of the free molecule. Molden [42] was used as graphical interface.

3. Results and discussion

3.1 Conformations of cinchonidine on platinum

In the competent literature virtually all modeling studies on the CD–platinum system are based on the assumption that the Open (3) conformation of CD, most populated in apolar solvents [43], can also account for enantioselectivity on platinum. Experimental evidence in favor of this conclusion has not yet been produced due to the lack of suitable spectroscopic techniques, therefore DFT calculations could help the understanding of the local geometry of the chiral sites [27]. Figure 2 shows the calculated conformations of CD when adsorbed on platinum while table 1 shows the relative energies, calculated with reference to the SC(1). Note that of the six surface conformers the first three SC(1), surface open(4) (SO(4)) and surface quinuclidine bound(1) (SQB(1)) can be obtained from each other by rotation of the τ_1 and τ_2 torsional angles. To obtain the other three conformers (surface closed(2) (SC(2)), surface open(3) (SO(3)) and surface quinuclidine bound(2) (SQB(2))), the desorption and rotation (around τ_1) of the quinoline ring is required. This shows that the alkaloid after adsorption can have a rather complex behaviour, in principle different from that found in a solvent. The relative energies of the analogous conformers are not as expected in solution (SC(1), SC(2) and SQB(1) result more stable than SO(3)) and additionally new constraints are present on the metal that can bias the conformational equilibrium. The equilibrium between SC(1), SO(4) and SQB(1) and SC(2), SO(3) and SQB(2) must pass through a desorption step, so that rotation at τ_1 is not free as in solution and furthermore quinuclidine can bind to platinum, thus setting a constraint not present in solution. In order to further understand the role of the surface conformers, also the possibility of interaction with the substrate should be considered. The prochiral ketones are hydrogenated by activated surface hydrogen, therefore in contact with the metal. Asymmetric hydrogenation can only occur in proximity of the alkaloid, where the chiral space is formed. The tertiary nitrogen of quinuclidine has been shown to be critical for asymmetric hydrogenation and it has been proposed that its interaction with the substrate occurs via hydrogen bonding [44], or alternatively by



a) SC(1) b) SO(4) c) SQB(1)
d) SC(2) e) SO(3) f) SQB(2)

Figure 2. Conformations of CD on platinum.

Table 1. Relative energies $\Delta E_{\text{el.}}$ calculated with respect to the energy of the structure SC(1) (set to zero) and values of the angles of rotation τ_1 and τ_2 for the surface conformations. Positive energy values stand for less stable structure than the reference. Adsorption energies ($E_{\text{Ads.}}$) were calculated as specified in Section 2. Energies in kcal/mol and angles in degrees.

	SO(3)	*SO(4)*	*SC(1)*	*SC(2)*	*SQB(1)*	*SQB(2)*
$\Delta E_{\text{el.}}$	1.7	3.9	0.0	0.5	0.2	6.6
τ_1	58	300	302	69	120	310
τ_2	134	126	56	61	171	287
$E_{\text{Ads.}}$	31.3	29.6	33.0	32.5	32.8	26.4

nucleophylic attack [45]. The closed conformations (SC(1) and SC(2)) exhibit a tertiary amino group that is too far from the metal site where hydrogenation occurs. Nevertheless closed conformers can generate open conformers (SO(4) and SO(3)) by rotation around τ_2. Successive rotation around τ_1 can then lead to the conformations where the quinuclidine is in contact with the platinum. It seems likely that those structures where the quinuclidine lies very close to the surface play a major role in selectively binding the substrate. This can occur by hydrogen uptake of the quinuclidine nitrogen, which has been shown to be a favourable process [26], which makes hydrogen bonding to the substrate possible also in the absence of a protic solvent. The SO(3) and SO(4) conformations also have a quinuclidine moiety which is rather distant from the catalytic site, but a simple rotation on τ_1 leads to surface conformers where the tertiary nitrogen is close to the surface. When analyzing such conformers it results that SQB(1), generated by the SO(4) after rotation of τ_1, is considerably more stable than SQB(2), which can be generated by the SO(3). This is due to the steric repulsion that occurs in SQB(2) between the anchoring group and the quinuclidine moiety. In conclusion, the most likely occuring active surface conformation is SQB(1). In the real system formed by the metal, the modifier and the solvent, all conformations are present at equilibrium, but calculations would predict a major fractional coverage of the SQB(1) conformer, which also has a correct positioning of the critical functional groups. The modeling presented suggests that the SQB(1) surface conformation is more likely to be responsible for selectivity (typically leading to an -(*R*) enantiomeric excess in the hydrogenation of prochiral ketones) than the SO(3), which is usually regarded as the key conformation, and widely used for modeling purposes.

3.2 Conformations of O-phenyl-cinchonidine on platinum

As mentioned in the introduction, CD ethers having a phenyl moiety bound to the oxygen (scheme 1) show an interesting behavior when used as surface modifiers in enantioselective hydrogenation. In fact OPhCD has the same absolute configuration as CD, but produces the -(*S*) enantiomer instead of the -(*R*) during enantioselective hydrogenation of α-ketoesters [46]. The same behavior occurs also when the phenyl moiety is replaced by a 3,5-dimethylphenyl moiety, while another inversion of selectivity occurs when the phenyl ring is 3,5-bis-trifluoromethylated, again leading to an -(*R*) enantiomeric excess [46]. This series of modifiers shows that the geometry of the chiral sites can be changed by derivatization of CD and that the kind of derivatization is critical for enantioselectivity. Of particular interest is the fact that *O*-(3,5-dimethylphenyl)-cinchonidine (dMePhOCD) is sterically very similar to *O*-[3,5-bis(trifluoromethyl)phenyl]-cinchonidine (tFPhOCD), but affords the opposite enantiomer. Inversion of enantioselectivity cannot be due to a different steric hindrance of the substituents, but must have its origin in their different electronic structure. As a first step towards the understanding of the geometry of the chiral sites generated by the OPhCD, this was adsorbed on platinum, as shown in figure 3. Calculated conformations SO(3) and SO(4) (figure 3) show the effect of the interaction of the phenyl ring to platinum: a partial chemisorption of the aromatic ring occurs for both structures. The adsorption energy of SO(3) for the OPhCD is almost identical (31.9 kcal/mol) to that of the SO(3) of CD (see table 1). This indicates that the phenyl ring has both stabilizing and destabilizing effects on adsorption, in almost equal amounts. Binding of the phenyl to platinum is stabilizing, but distortion of the equilibrium conformation in vacuum (figure 3) is destabilizing. Overall, the adsorption energy of this conformation does not change compared to that of CD. Experimentally, it has been shown that OPhCD can be replaced by competition with CD, when both modifiers are present in the reaction environment [17]. The reason for this behavior can be evinced by the comparison of the Open(3) and Open(4) conformations in vacuum with the SO(3) and SO(4) conformations, shown in figure 3.

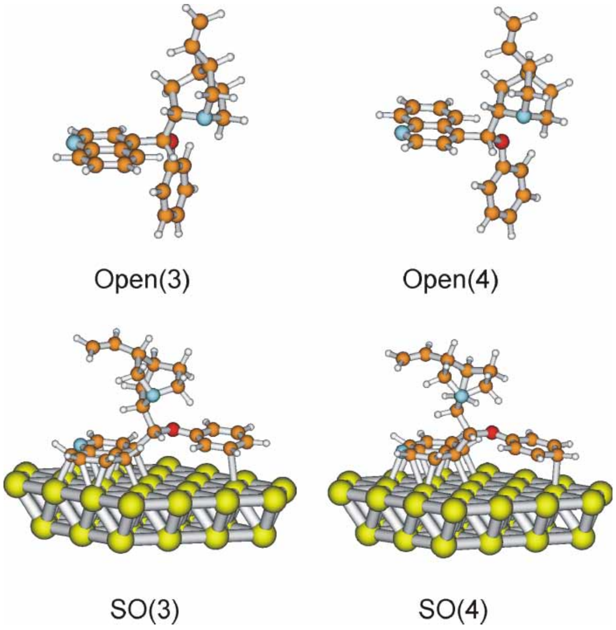


Figure 3. Open(3) and Open(4) conformations of OPhCD and the correspondent SO(3) and SO(4) conformations on platinum.

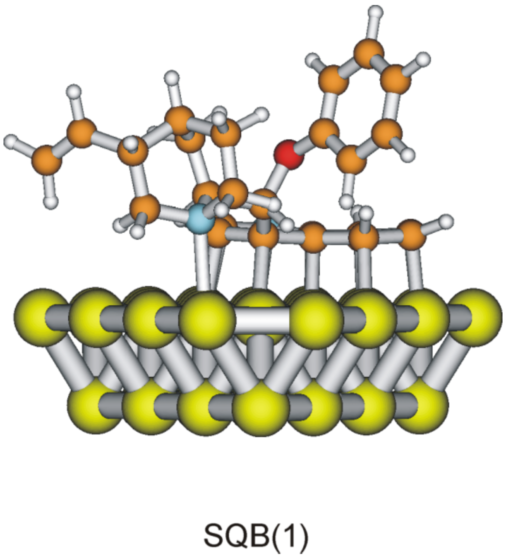


Figure 4. SQB(1) conformations of OPhCD on platinum.

The formation of the strong adsorbing species should be slow, since it requires distortion of the conformations present in solution. As a consequence, transient adsorbed (weakly bound) species occupy the surface, which can be easily displaced by CD in a competition for adsorption sites, since the latter finds more easily the way to strongly bound metal sites (in simpler terms, its strong adsorption on platinum is less hindered). To summarize, calculations suggest that the competition for metal sites is favourable to CD because of entropic rather than enthalpic factors, since the estimate of the heat of adsorption gives similar values for both molecules. It is also interesting to note that in the case of OPhCD, SO(3) and SO(4) have almost exactly the same electronic energy, while in the case of CD SO(3) is almost 2 kcal/mol more stable than SO(4) (table 1). Open (3) and Open(4) have been shown to have different stabilities in vacuum, with a difference in electronic energy of circa 3 kcal/mol in favour of the Open(3) [47]. This shows that the surface has the effect of leveling the stabilities of conformers. Seen from another standpoint, the surface can accomodate an Open(4) conformation better than on Open(3). This is due to the subtle balance of binding and repulsive interactions that characterize the presence of an *O*-substituent in proximity of the surface and also in proximity of the anchoring group.

Also, the SQB(1) structure for OPhCD was calculated (figure 4) and resulted *circa* 2 kcal/mol more stable than the SO(3) and SO(4). This shows that the trend of increasing stability of the conformers for which the quinuclidine moiety is in contact with the metal holds also for OPhCD. Another interesting observation is that all the adsorbed structures of OPhCD shown have the phenyl moiety close to the metal, either partially adsorbed with the plane almost parallel to the surface (figure 3), or with the plane of the ring perpendicular to the surface (figure 4). As already stated, the prochiral substrate must be adsorbed near to the surface modifier in order to be selectively hydrogenated, therefore the presence of the phenyl ring in proximity of the chiral space is most likely to be responsible for the inversion of enantioselectivity of OPhCD with respect to CD.

3.3 The adsorption of anisoles on platinum

To understand the different behavior of dMePhOCD and tFPhOCD when used as surface modifiers in enantioselective hydrogenation, the effect of substitution at the phenyl ring in relation to its adsorption properties on platinum was investigated [41]. Substituted anisoles were used as model compounds, due to their similarity to the *O*-phenyl ether substituents of the alkaloids in study. The adsorption of 3,5-dimethylanisole (DMA) and 3,5-bis-(trifluoromethyl)-anisole (tFDMA) was studied and compared to that of benzene and anisole. Details of these calculations are given elsewhere [41], here we only mention that a smaller cluster of 31 platinum atoms was used, since the adsorbed molecules occupy less surface area on the metal. Figure 5 shows the most stable adsorption site (bridge) for anisole, DMA and tFDMA. At the same level of theory as used for the previously shown calculations on CD and OPhCD, the values for the adsorption energies of anisole, DMA and tFDMA are 25.7, 23.3 and 15.6 kcal/mol respectively. While the first two have very similar interaction energy with the metal, the trifluoromethylated compound has a lower adsorption

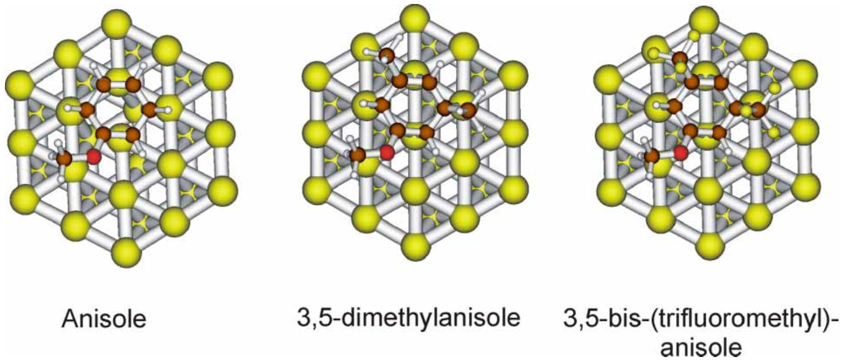


Figure 5. Adsorption on bridge sites of anisole, DMA and tFDMA.

energy by *circa* 10 kcal/mol. This indicates that tFPhOCD should have surface conformations where the contribution of the phenyl moiety to adsorption is less important than in OPhCD and dMeOPhCD. It is of course not simple to draw all the consequences by this strikingly different behavior of the fluorinated moiety, since a complete study of all surface conformers of the *O*-phenyl modifiers would be necessary to clarify to which extent and how the chiral sites are affected. What seems clear is that this difference in the adsorption behaviour can greatly affect the fractional coverage of surface conformers, which we have seen in the case of OPhCD is very sensitive to derivatization and can also invert the relative population of stable conformers on the metal thus affecting its selectivity. The conformational changes in the adsorbed modifier are most probably the origin of the switching back of the enantioselective properties of platinum to an -(*R*) inducing reactivity, when tFPhOCD is used as surface modifier.

4. Conclusions

Understanding the local geometry of chiral sites formed by adsorption of modifiers on platinum would be very useful for the design of tailored catalysts and enantio-switching materials. Experimental techniques apt to disclose this kind of information in sufficient detail are not yet available and computational modeling can help to investigate complex structural features of highly flexible adsorbates. It has been shown that the structure of cinchona alkaloids after adsorption is characterized by several minima, of which the most likely to be responsible for enantioselection interacts with the metal also via the quinuclidine moiety. Also, the conformational mobility about the τ_1 angle, typical of the cinchona alkaloids in solution is partially hindered by adsorption. CD phenyl-ethers, that show a different enantioselectivity as surface modifers, should also have a different fractional coverage of surface species, because the phenyl moiety can contribute in different proportion to binding the metal according to ring substitution. The complex conformational equilibria that can arise are not fully uncovered, but the study of model systems (substituted anisoles) point to a possible correlation between the loss of adsorption energy calculated for the 3-5-bis-trifluoromethylanisole on platinum and the switch of enantioselectivity observed for the CD ether bearing this fluorinated group bound to the oxygen. The change in fractional coverage of surface conformers could be the cause of the inversion of selectivity between dMeOPhCD and tFPhOCD.

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